Chemistry of Heterocyclic Compounds, Vol. 34, No. 6, 1998

MOLECULAR AND CRYSTAL STRUCTURE OF 1-METHYLMORPHOLINIUM 6-METHYL-4-PHENYL-3-CYANO-5-ETHOXYCARBONYL-1,4-DIHYDRO-2-PYRIDINESELENOLATE

V. N. Nesterov and V. D. Dyachenko

The structure of 1-methylmorpholinium 6-methyl-4-phenyl-3-cyano-5-ethoxycarbonyl-1,4-dihydro-2-pyridineselenolate was studied using x-ray diffraction analysis. It was found that the 1,4-dihydropyridine ring has a boat conformation, and the plane of the pseudoaxial phenyl substituent is perpendicular to the bottom of this boat. In the anion, the C−Se bond length, which is 1.882(2) Å, indicates that the negative charge is formally located on the Se atom. The anions and cations of the salt in the crystal are linked by intermolecular hydrogen bonds.

Continuing the study of the structure of salts of chalcogen-containing azines [1-3], we have for the first time carried out an x-ray diffraction study of 1-methylmorpholinium 6-methyl-4-phenyl-3-cyano-5-ethoxycarbonyl-1,4-dihydro-2-pyridineselenolate (I). Figure 1 shows the general form of the anion and cation of salt I, and the bond angles and valence angles are given in Tables 1 and 2.

According to the data of the Cambridge Crystallographic Database [4] (including June, 1997), the literature lacks data on the structure of selenium-containing azinium salts. In the anion of the investigated salt, the 1,4-dihydropyridine ring has a flattened-boat conformation: the $N_{(1)}$ and $C_{(4)}$ atoms protrude from the plane of the remaining four atoms of the ring (the plane is true to ±0.025 Å) by 0.133 Å and 0.311 Å, respectively; this corresponds to a bending of the heterocycle along the $C_{(2)}\cdots C_{(6)}$ line by 11.7°, $C_{(3)}\cdots C_{(5)}$ by 20.7°, and $N_{(1)}\cdots C_{(4)}$ by 20.0°. Earlier, we observed a similar conformation of the 1,4-dihydropyridine ring in thiolates [1-3]. The pseudoaxial phenyl substituent is practically perpendicular to the bottom of the heterocycle boat: the dihedral angle between them is 89.2°.

Earlier, in a study of thiolates, we assumed that the negative charge is formally located on the S atom [1-3]. Similarly, in the anion of salt I, the negative charge is also formally on the Se atom, as indicated by the $C_{(2)}-Se$ bond length (1.882(2) Å), which appreciably exceeds the length of the conjugated double bond C=Se (1.80(1) Å) in substituted pyridine-2-(1H)-selenone [5] and 1-methylpyridine-2-selenone (1.834(5) Å) [6], but is appreciably shorter than the $C_{sp^2}-Se$ single bond (1.902(9)-1.921(4) Å) in substituted 2-allylselenopyridines [7, 8]. The indicated localization of charge is also confirmed by the fact that alkylation of selenolates takes place strictly at the selenium atom [9]. The N-methylmorpholinium cation has a regular chair conformation with an equatorial orientation of the methyl group. In the virtually planar fragment $Se-C_{(2)}=C_{(3)}-C_{(17)}\equiv N_{(2)}$, conjugation causes an appreciable redistribution of the bond lengths (Table 1) in comparison to the standard values. In the virtually planar fragment $C_{(6)}=C_{(5)}-C_{(8)}=O_{(1)}$ (the torsional angle $C_{(6)}$, $C_{(5)}$, $C_{(8)}$, $O_{(1)}$ is 16.9°), conjugation also causes a certain redistribution of the bond lengths in comparison to the standard values [10]. The observed orientation of the carbonyl group leads to a reduced nonvalence contact $C_{(7)}-H_{(71)}\cdots O_{(1)}$, which according to [11] can be regarded as an intramolecular hydrogen bond of the type C−H···O with the parameters $C_{(7)}\cdots O_{(1)}$ 2.882(3), $C_{(7)}-H_{(71)}$ 0.91(2), $H_{(71)}\cdots O_{(1)}$ 2.28(2) Å, angle $C_{(7)}-H_{(71)}\cdots O_{(1)}$ 123(2)°.

In the crystal, the intermolecular hydrogen bond $N_{(3)}-H_{(3)}\cdots Se(x-1, y, z)$ ($N_{(3)}\cdots Se$ 3.305(3), $N_{(3)}-H_{(3)}$ 0.91(2), $H_{(3)}\cdots Se$ 2.40(2) Å), angle $N_{(3)}-H_{(3)}\cdots Se$ 175(2)°) links the cations and anions of salt I. The weaker intermolecular H bond $N_{(1)}-H_{(1)}\cdots Se(1, -x, -y, -z)$ ($N_{(1)}\cdots Se$ 3.718(3), $N_{(1)}-H_{(1)}$ 0.86(2), $H_{(1)}\cdots Se$ 2.90(2) Å, angle $N_{(1)}-H_{(1)}\cdots Se$ 158(2)°) links the anions into centrosymmetric dimers (Fig. 2).

A. N. Nesmeyanov Institute of Heteroorganic Compounds, Russian Academy of Sciences, Moscow 117813, Russia. T. G. Shevchenko Lugansk State Pedagogical Institute, Lugansk 348011, Ukraine. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 6, pp. 785-789, June, 1998. Original article submitted August 4, 1997.

0009-3122/98/3406-0683$20.00

TABLE 1. Bond Lengths (d) in the Molecule of Compound I

Bond	*d*, Å	Bond	*d*, Å
Se—$C_{(2)}$	1,882(2)	$C_{(4)}$—$C_{(11)}$	1,522(3)
$O_{(1)}$—$C_{(8)}$	1,212(3)	$C_{(4)}$—$C_{(5)}$	1,523(3)
$O_{(2)}$—$C_{(8)}$	1,344(3)	$C_{(5)}$—$C_{(6)}$	1,354(3)
$O_{(2)}$—$C_{(9)}$	1,453(3)	$C_{(5)}$—$C_{(8)}$	1,478(3)
$O_{(3)}$—$C_{(18)}$	1,421(4)	$C_{(6)}$—$C_{(7)}$	1,498(3)
$O_{(3)}$—$C_{(21)}$	1,424(3)	$C_{(9)}$—$C_{(10)}$	1,499(4)
$N_{(1)}$—$C_{(2)}$	1,380(3)	$C_{(11)}$—$C_{(16)}$	1,384(3)
$N_{(1)}$—$C_{(6)}$	1,392(3)	$C_{(11)}$—$C_{(12)}$	1,396(3)
$N_{(2)}$—$C_{(17)}$	1,151(3)	$C_{(12)}$—$C_{(13)}$	1,379(4)
$N_{(3)}$—$C_{(22)}$	1,486(3)	$C_{(13)}$—$C_{(14)}$	1,362(5)
$N_{(3)}$—$C_{(20)}$	1,492(3)	$C_{(14)}$—$C_{(15)}$	1,387(4)
$N_{(3)}$—$C_{(19)}$	1,501(3)	$C_{(15)}$—$C_{(16)}$	1,375(4)
$C_{(2)}$—$C_{(3)}$	1,368(3)	$C_{(18)}$—$C_{(19)}$	1,493(4)
$C_{(3)}$—$C_{(17)}$	1,416(3)	$C_{(20)}$—$C_{(21)}$	1,497(4)
$C_{(3)}$—$C_{(4)}$	1,531(3)		

TABLE 2. Valence Angles ω in the Molecule of Compound I

Angle	ω (deg.)	Angle	ω (deg)
$C_{(8)}$—$O_{(2)}$—$C_{(9)}$	116,5(2)	$C_{(5)}$—$C_{(6)}$—$C_{(7)}$	126,9(2)
$C_{(18)}$—$O_{(3)}$—$C_{(21)}$	109,2(2)	$N_{(1)}$—$C_{(6)}$—$C_{(7)}$	113,2(2)
$C_{(2)}$—$N_{(1)}$—$C_{(6)}$	123,3(2)	$O_{(1)}$—$C_{(8)}$—$O_{(2)}$	122,1(2)
$C_{(22)}$—$N_{(3)}$—$C_{(20)}$	112,2(2)	$O_{(1)}$—$C_{(8)}$—$C_{(5)}$	126,6(2)
$C_{(22)}$—$N_{(3)}$—$C_{(19)}$	111,1(2)	$O_{(2)}$—$C_{(8)}$—$C_{(5)}$	111,3(2)
$C_{(20)}$—$N_{(3)}$—$C_{(19)}$	110,2(2)	$O_{(2)}$—$C_{(9)}$—$C_{(10)}$	106,8(2)
$C_{(3)}$—$C_{(2)}$—$N_{(1)}$	117,6(2)	$C_{(16)}$—$C_{(11)}$—$C_{(12)}$	117,3(2)
$C_{(3)}$—$C_{(2)}$—Se	126,4(2)	$C_{(16)}$—$C_{(11)}$—$C_{(4)}$	121,7(2)
$N_{(1)}$—$C_{(2)}$—Se	116,1(1)	$C_{(12)}$—$C_{(11)}$—$C_{(4)}$	120,8(2)
$C_{(2)}$—$C_{(3)}$—$C_{(17)}$	121,7(2)	$C_{(13)}$—$C_{(12)}$—$C_{(11)}$	120,9(3)
$C_{(2)}$—$C_{(3)}$—$C_{(4)}$	122,1(2)	$C_{(14)}$—$C_{(13)}$—$C_{(12)}$	121,0(3)
$C_{(17)}$—$C_{(3)}$—$C_{(4)}$	116,1(2)	$C_{(13)}$—$C_{(14)}$—$C_{(15)}$	119,0(3)
$C_{(11)}$—$C_{(4)}$—$C_{(5)}$	113,2(2)	$C_{(16)}$—$C_{(15)}$—$C_{(14)}$	120,4(3)
$C_{(11)}$—$C_{(4)}$—$C_{(3)}$	109,2(2)	$C_{(15)}$—$C_{(16)}$—$C_{(11)}$	121,4(2)
$C_{(5)}$—$C_{(4)}$—$C_{(3)}$	109,5(2)	$N_{(2)}$—$C_{(17)}$—$C_{(3)}$	173,8(2)
$C_{(6)}$—$C_{(5)}$—$C_{(8)}$	121,7(2)	$O_{(3)}$—$C_{(18)}$—$C_{(19)}$	111,4(2)
$C_{(6)}$—$C_{(5)}$—$C_{(4)}$	120,9(2)	$C_{(18)}$—$C_{(19)}$—$N_{(3)}$	110,5(2)
$C_{(8)}$—$C_{(5)}$—$C_{(4)}$	117,3(2)	$N_{(3)}$—$C_{(20)}$—$C_{(21)}$	110,8(2)
$C_{(5)}$—$C_{(6)}$—$N_{(1)}$	119,9(2)	$O_{(3)}$—$C_{(21)}$—$C_{(20)}$	111,2(2)

EXPERIMENTAL

Salt I was obtained and characterized in [9].

X-Ray Diffraction Analysis of 1-Methylmorpholinium 6-Methyl-4-phenyl-3-cyano-5-ethoxycarbonyl-1,4-dihydro-2-pyridineselenolate (I). $C_{21}H_{27}N_3O_3Se$. Crystals of compound I are triclinic, at 20°C: a = 9.311(1), b = 11.550(2), c = 11.656(2) Å, α = 93.39(1), β = 110.69(1), γ = 109.09(1)°, V = 1086.3(3) Å^3, d_{calc} = 1.371 g/cm^3, Z = 2, space group P-1. The unit cell parameters and intensities of 6109 independent reflections were measured on a Siemens P3/PC four-circle automatic diffractometer (λMoKα, graphite monochromator, $\theta/2\theta$, scanning to θ_{max} = 27°). The structure was solved by using the direct method technique, which revealed all atoms except hydrogen, and was refined by means of full-matrix least-squares analysis using anisotropic parameters for all atoms except hydrogen. All the hydrogen atoms were objectively revealed in a different Fourier map and refined isotropically. The final values of the agreement factors were R_f = 0.039 using 4607 independent reflections with $I > 2\sigma(I)$ and R_{w2} = 0.089 using 5348 independent reflections. All the calculations were carried out using the SHELXTL PLUS and SHELXL-93 programs (PC version). The coordinates and isotropic (for nonhydrogen atoms — equivalent) thermal parameters of the atoms are listed in Table 3.

TABLE 3. Coordinates ($\times 10^4$) and Isotropic (for certain atoms, equivalent) Thermal Parameters of Atoms in the Molecule of Compound I

Atom	x	y	z	$U_{(eq)}$
1	2	3	4	5
Se	4797(1)	1987(1)	-6(1)	41(1)
$O_{(1)}$	106(2)	-1935(2)	2742(2)	56(1)
$O_{(2)}$	-384(2)	-179(1)	2948(2)	46(1)
$O_{(3)}$	-139(2)	3879(2)	3692(2)	64(1)
$N_{(1)}$	3302(2)	47(2)	995(2)	42(1)
$N_{(2)}$	2738(3)	4029(2)	1246(3)	61(1)
$N_{(3)}$	-2648(2)	4606(2)	2038(2)	40(1)
$C_{(2)}$	3532(2)	1276(2)	905(2)	34(1)
$C_{(3)}$	2825(2)	1857(2)	1476(2)	35(1)
$C_{(4)}$	2109(2)	1290(2)	2401(2)	35(1)
$C_{(5)}$	1557(2)	-127(2)	2104(2)	36(1)
$C_{(6)}$	2185(3)	-680(2)	1449(2)	38(1)
$C_{(7)}$	1775(4)	-2053(2)	1100(3)	53(1)
$C_{(8)}$	373(3)	-863(2)	-2606(2)	39(1)
$C_{(9)}$	-1630(3)	-816(2)	3412(3)	46(1)
$C_{(10)}$	-2409(4)	86(3)	3608(4)	63(1)
$C_{(11)}$	3386(3)	1874(2)	3729(2)	36(1)
$C_{(12)}$	3352(4)	2889(3)	4418(3)	59(1)
$C_{(13)}$	4587(5)	3489(3)	5578(3)	75(1)
$C_{(14)}$	5859(4)	3095(3)	6096(3)	61(1)
$C_{(15)}$	5900(3)	2074(3)	5437(3)	54(1)
$C_{(16)}$	4683(3)	1481(2)	4272(2)	45(1)
$C_{(17)}$	2821(3)	3061(2)	1312(2)	41(1)
$C_{(18)}$	-330(4)	3893(3)	2430(3)	64(1)
$C_{(19)}$	-1018(3)	4845(3)	1934(3)	55(1)
$C_{(20)}$	-2493(3)	4470(3)	3337(2)	48(1)
$C_{(21)}$	-1720(4)	3536(3)	3757(3)	60(1)
$C_{(22)}$	-3293(4)	5595(3)	1627(4)	60(1)
$H_{(1)}$	3692(34)	-320(26)	580(26)	51(7)
$H_{(3)}$	-3378(34)	3868(27)	1515(25)	53(7)
$H_{(4)}$	1135(27)	1497(20)	2304(20)	31(5)
$H_{(71)}$	1091(56)	-2589(43)	1399(42)	116(15)
$H_{(72)}$	1227(71)	-2390(54)	286(57)	160(22)
$H_{(73)}$	2589(68)	-2295(50)	1222(50)	143(20)
$H_{(91)}$	-1089(32)	-1090(25)	4177(25)	48(7)
$H_{(92)}$	-2360(36)	-1565(29)	2783(27)	59(8)
$H_{(101)}$	-3171(47)	-242(35)	4001(34)	90(11)
$H_{(102)}$	-3070(45)	261(35)	2677(38)	92(11)
$H_{(103)}$	-1587(45)	799(36)	4150(33)	80(11)
$H_{(12)}$	2478(41)	3134(31)	4106(30)	74(10)
$H_{(13)}$	4584(45)	4147(37)	5988(35)	91(11)
$H_{(14)}$	6628(39)	3466(30)	6902(31)	68(9)
$H_{(15)}$	6756(42)	1758(32)	5765(31)	78(10)
$H_{(16)}$	4645(37)	792(30)	3812(28)	66(9)
$H_{(181)}$	-1046(35)	3065(28)	1966(26)	52(7)
$H_{(182)}$	743(45)	4123(33)	2504(32)	82(10)
$H_{(191)}$	-307(37)	5661(29)	2423(28)	60(8)
$H_{(192)}$	-1191(35)	4821(27)	1077(28)	58(8)
$H_{(202)}$	-3616(36)	4234(27)	3335(26)	58(8)
$H_{(211)}$	-2409(38)	2793(30)	3232(29)	61(9)
$H_{(212)}$	-1485(42)	3540(33)	4663(35)	82(10)
$H_{(221)}$	-3316(41)	5636(32)	802(34)	75(10)
$H_{(222)}$	-2540(41)	6337(33)	2129(31)	72(9)
$H_{(223)}$	-4338(43)	5449(31)	1669(30)	71(9)

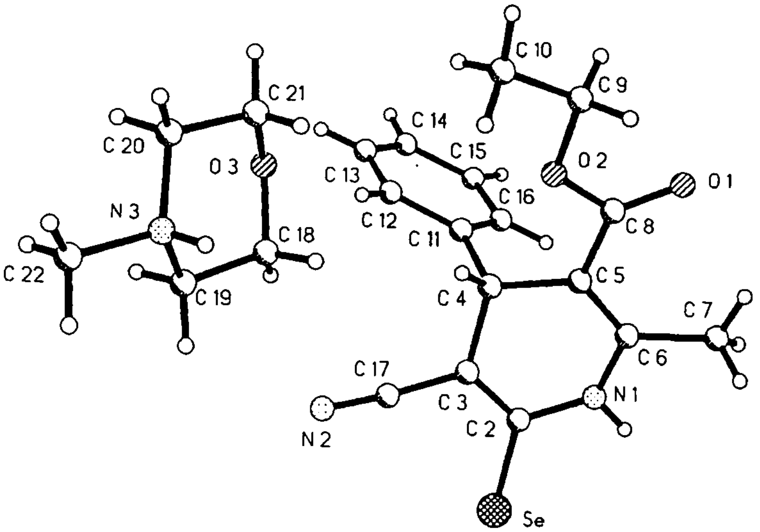

Fig. 1. General form of the cation and anion of salt I.

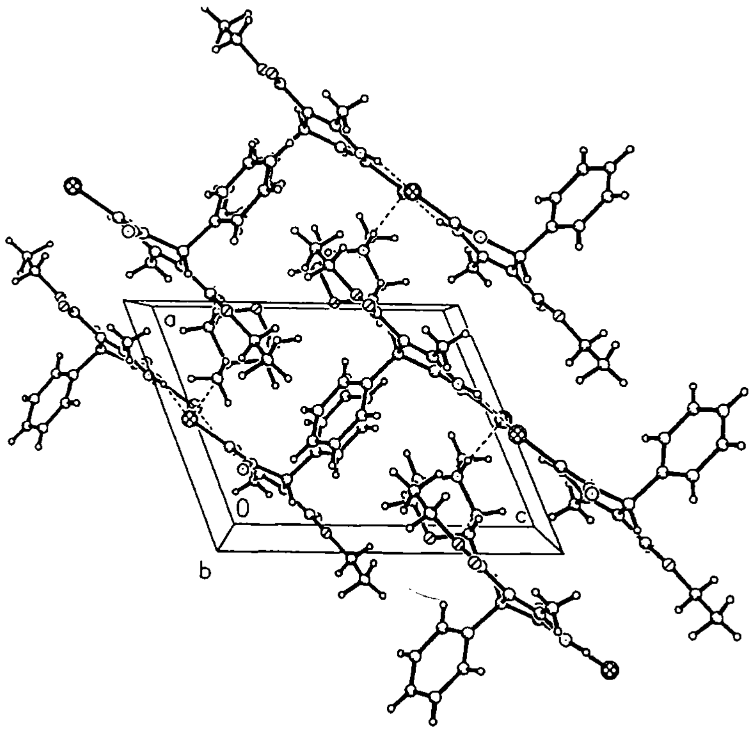

Fig. 2. Projection *ac* of the crystal structure of salt I. Dashed lines represent N–H···Se intermolecular hydrogen bonds.

The work was supported financially by the Russian Fund for Basic Research (Project No. 97-03-33783a). The authors thank the Russian Fund for Basic Research for partial payment of the license for use of the Cambridge Crystallographic Database (Project No. 96-07-89187).

REFERENCES

1. V. N. Nesterov, V. E. Shklover, Yu. T. Struchkov, Yu. A. Sharanin, A. M. Shestopalov, and L. A. Rodinovskaya, Acta Crystallogr., **C41**, 1191 (1985).

2. V. D. Dyachenko, S. G. Krivokolysko, V. N. Nesterov, Yu. T. Struchkov, and V. P. Litvinov, Izv. Akad. Nauk, Ser. Khim., No. 10, 2535 (1996).
3. V. N. Nesterov, S. G. Krivokolysko, V. D. Dyachenko, V. V. Dotsenko, and V. P. Litvinov, Izv. Akad. Nauk, Ser. Khim., No. 5, 1029 (1997).
4. Cambridge Crystallographic Database, Release 1997, Cambridge.
5. V. N. Nesterov, V. E. Shklover, Yu. T. Struchkov, V. P. Litvinov, E. É. Apenova, V. Yu. Mortikov, and Yu. A. Sharanin, Izv. Akad. SSSR, Ser. Khim., No. 2, 477 (1988).
6. T. Srikrishnan, Acta Crystallogr., **C44**, 290 (1988).
7. V. N. Nesterov, V. D. Dyachenko, Yu. A. Sharanin, and Yu. T. Struchkov, Izv. Akad. Nauk, Ser. Khim., No. 1, 122 (1994).
8. V. N. Nesterov, V. E. Shklover, Yu. T. Struchkov, V. D. Dyachenko, and Yu. A. Sharanin, Izv. Akad. Nauk SSSR, Ser. Khim., No. 11, 2585 (1989).
9. V. D. Dyachenko and Yu. A. Sharanin, Zh. Obshch. Khim., **61**, No. 4, 948 (1991).
10. F. H. Allen, O. Kennard, D. G. Watson, L. Brammer, A. G. Orpen, and R. Taylor, J. Chem. Soc. Perkin Trans. II, No. 2, 1 (1987).
11. Z. Berkovitch-Yellin and L. Leiserowitz, Acta Crystallogr., **C40**, 159 (1984).